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ANNUAL SUMMARY REPORT .

FAR INFRARED SPECTRA OF CRYSTALS AND SOLIDS  
IN A LARGE RANGE OF TEMPERATURES.

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Far Infrared spectra of 11 solids at liquid helium temperature and 7 at room temperature.

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This is a summary of the work described in administrative reports n° 1 to 7, with some additives covering the period from 31/1/1963 to 30/4/1963.

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I - WORK EXECUTED DURING THE FIRST TWO YEARS PERIOD . (1/3/1961 to 30/4/ 1963). -

1. - Instrumentation. -

- a) Development of Far Infrared techniques at low temperature : the helium is recycled and we established the connexion of our laboratory to an outside gazometer at the end of December 1961. Our first liquid helium cryostat was ready since October 1961 (Fig. 18). There has been some difficulties to locate accurately the cryostat inside the evacuated spectrometer (Fig. 1).
- b) Development of a polariser (Fig. 2): we use a pile of 20 sheet of polyethylene (thickness 30 microns).

2. - Far Infrared absorption spectra at liquid helium temperature. -

We got the first spectra at liquid helium temperature in May 1962 and during the last 10 months we studied :

Ge (Fig. 3 - 4) , Quartz (Fig. 5), Silica (Fig. 21), I Cs (Fig. 9)  $\text{Al}_2\text{O}_3$ ,  $\text{F}_2\text{Ca}$  (Fig. 12),  $\text{F}_2\text{Sr}$  (Fig. 12),  $\text{F}_3\text{Tm}$  (Fig. 13),  $\text{Cu}_2\text{O}$  (Fig. 15), Te Hg.

Except for Germanium, this seems to be the first collection of Far Infrared data at liquid helium temperature.

3. - Far Infrared absorption spectra at room temperature. -

At room temperature we studied  $\text{SnI}_4$  (Fig. 14),  $\text{Cu}_2\text{O}$  (Fig. 15 - 16), Gypsum,  $(\text{CN})_2\text{Hg}$ ,  $\text{Cl}_2\text{Hg}$ ,  $\text{Cl}_2\text{Hg}_2$ , NaCl and all the above mentioned crystals. Calcite ( $\text{CO}_3\text{Ca}$ ) (Fig. 19) and Siderose ( $\text{CO}_3\text{Fe}$ ) (Fig. 20) have been studied with polarised radiations.

4. - Theory and Applications. -

- a) The need for a large collection of well established accurate infrared spectra of solids has been stressed by some scientists (réf. 1 for instance), in

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order to develop a theory of lattice dynamics which would lie on solid experimental basis. It is too soon to try to relate completely our spectra to lattice dynamics.

- b) In a first stage we try a LORENTZ one :  $P$  (Strength of the resonance),  $\delta$  width,  $\lambda_0$  (wavelength),  $\epsilon'_0$  (static dielectric constant).
- c) The general behaviour of the Far Infrared wing of the absorption band of single crystals at low temperature has a simple interpretation in quantum theory.
- d) The absorption coefficient of Quartz (single crystal) (Fig. 5) and molten quartz (glass) (Fig. 21) differ remarkably and their behaviour with temperature seems strikingly different.

## II - PRINCIPLE RESULTS. -

1. - Normal frequencies have been ascribed for :

I Cs (2) :  $\lambda_0 = 161$  microns;  $\text{Cu}_2\text{O}$  (5) : we cannot agree completely with PASTER-  
NIAK's assignment and we propose for the 2 Infrared active vibrations :  $\lambda_1 = 16,4$  microns ;  $\lambda_2 = 60$  microns; for  $\lambda_4$  (optically inactive) and  $\lambda_3$  (Raman ac-  
tive), we accept the assignments of PASTER-  
NIAK :  $\lambda_4 = 8,9$  microns;  $\lambda_3 = 55$  microns.

$\text{SnI}_4$  (3) ;  $(\text{CN})_2 \text{Hg}$  (5);  $\text{Cl}_2 \text{Hg}_2$  (5).

2. - Dichroism of the 70 microns absorption band of quartz (6). YAROSLAWSKI's sug-  
gestion of hydrogen bending of impurities ought to be considered.
3. - Effect of temperature on the Far Infrared lattice absorption spectra of single  
crystals (2 - 6 - 7).
  - a) The maximum of absorption is shifted to shorter wavelengths when the tempe-  
rature is decreased (see quartz,  $\text{Cu}_2\text{O}$ , ICs).
  - b) The transmission increases and this effect is highly more important on the  
low frequency wing of the absorption band (see Quartz,  $\text{Cu}_2\text{O}$ , ICs, Thulium  
fluoride).

The effect a) was generally awaited : the importance of effect b) was unspec-  
ted and our laboratory has probably been the first to establish it on a large  
number of single crystals. It is interesting with in two points of views :

.../....

- theoretical : it seems to confirm that vertical transitions from acoustical to optical branches of any wave vector are infrared active in a second order approximation. In other words any absorption on the low frequency wing of Far Infrared bands may be explained as a combination of one infrared photon with one acoustical phonon, to give one optical phonon. This absorption disappears at low temperatures when there is a lack of phonons in the crystal.
- technical : if it is true that at room temperature there is a great lack of materials transparent in the Far Infrared, the situation is reversed at low temperatures where a lot of single crystals get completely transparent. We have shown the possibility to select transparent hosts at liquid helium temperature where ions to be studied in the Far Infrared could be included (7) (Fig 22). Neodymium nitrate and Samarium nitrate have a lot of common lines ascribed to lattice vibrations and one specific line at 300 microns, ascribed to  $\text{Nd}^{3+}$ .

### III - BRIEF TECHNICAL DESCRIPTION OF THE WORK CONTEMPLATED ON FAR INFRARED SPECTRA OF CRYSTALS AND SOLIDS IN A LARGE RANGE OF TEMPERATURE DURING THE PERIOD OF EXTENSION (one year).

1. Far Infrared spectra of  $\text{CuCl}$  -  $\text{CuBr}$  -  $\text{CuI}$  -  $\text{NaCl}$  -  $\text{KBr}$  (single crystals) at various temperatures.
2. idem for  $\text{Ag}_2\text{O}$  compared to  $\text{Cu}_2\text{O}$ .
3. Idem for  $\text{La Br}_3$ ,  $\text{LaCl}_3$ ,  $\text{Nd Cl}_3$ ,  $\text{Pr Cl}_3$  (single crystals grown by Prof. Boris STOICHEFF).
4. We shall have to check again the spectra of silica and other glasses ( $\text{SiO}_2$ ) at low temperatures. It would be good to put the plate of glass between 2 plates of quartz when thermal conductivity is much higher. Up to now we have not found any difference between single crystals and pellets of powders. We shall try to get smaller particles and check again the spectra in order to find an explanation. It will be worthwhile to compare the spectra of Irtan and of a single crystal of  $\text{S Zn}$ .
5. Spectra of some molecular crystals (for instance  $\text{Cl}_2\text{Hg}_2$ ,  $(\text{CN})_2\text{Hg}$ , naphthalene etc....) at liquid helium temperature, where, up to now, there is not any experimental data.

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IV - REFERENCES. -

- (1) J. N. PLENDL, Phys. Rev. 123(1961) p. 1172.
- (2) Spectres d'absorption de monocristaux dans l'Infrarouge lointain (50 - 1600 microns) à la température de l'hélium liquide : iodure de Cesium, quartz, germanium et nitrate de néodyme , par MM. A. HADNI, J. CLAUDEL, E. DECAMPS, X. GERBAUX & P. STRIMER, Comptes Rendus, 255(1962) p. 1595.
- (3) Spectres d'absorption de  $\text{SnI}_4$  dans l'Infrarouge lointain, par X. GERBAUX & A. HADNI, Lettre à la Rédaction, J. de Phys. et le Rad. 23(1962) p. 877.
- (4) Spectres d'absorption de quelques composés minéraux dans l'Infrarouge moyen (1 à 30 microns) par Melle D., GRANDJEAN & A. HADNI, Publication du G.A.M.S. 1963, p. 44 - Colloque de Lyon en 1961.
- (5) Spectres d'absorption de quelques composés minéraux et organiques dans l'Infrarouge lointain (50 - 1000 microns) par A. HADNI, C. BOUSTER, E. DECAMPS, J.M. MUNIER & P. POINSOT , Publication du GAMS, p. 11 - Colloque de Lyon, 1961.
- (6) Instrumentation in the Far Infrared and applications of Far Infrared Spectra by A. HADNI, International Symposium on Far Infrared Spectroscopy , Cincinnati (Ohio) 1962. Spectrochimica Acta, 1963, 19, p. 793.
- (7) Matériaux transparents dans l'Infrarouge lointain (50 - 1600 microns), Application aux Masers optiques, par A. HADNI , B. WYNCKE, P. STRIMER, E. DECAMPS & J. CLAUDEL, Troisième Congrès International d'Electronique Quantique, Paris 1963.

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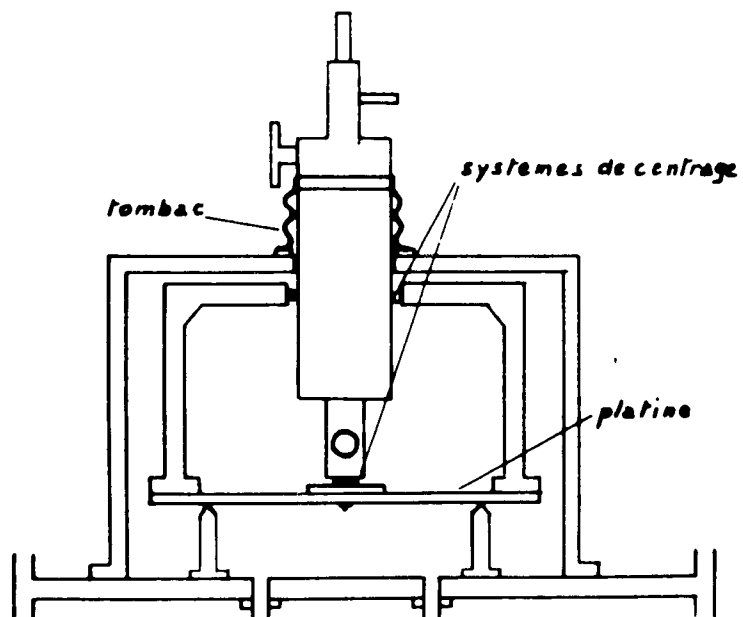


Fig. 1

Position du cryostat dans  
le spectroscope

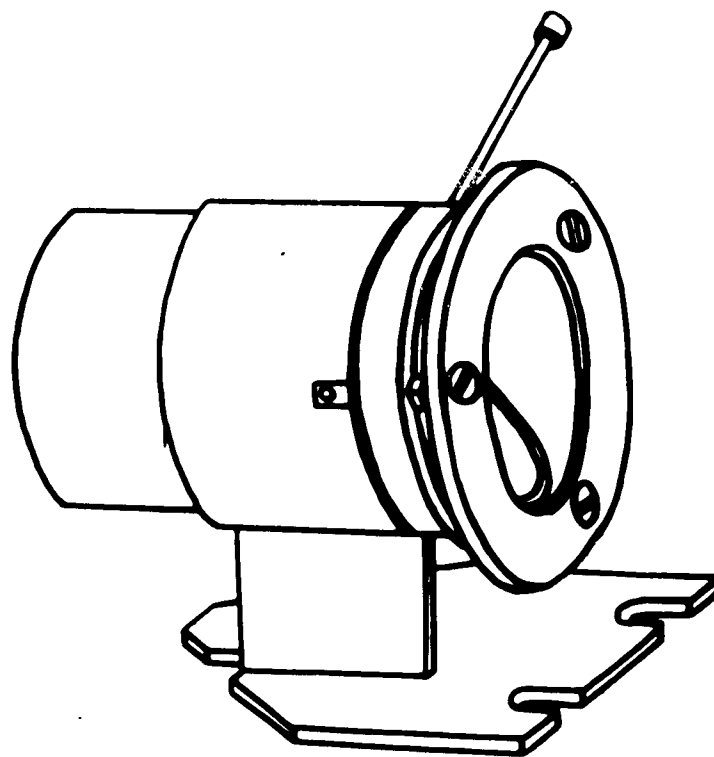


Fig. 2

Croquis du polariseur

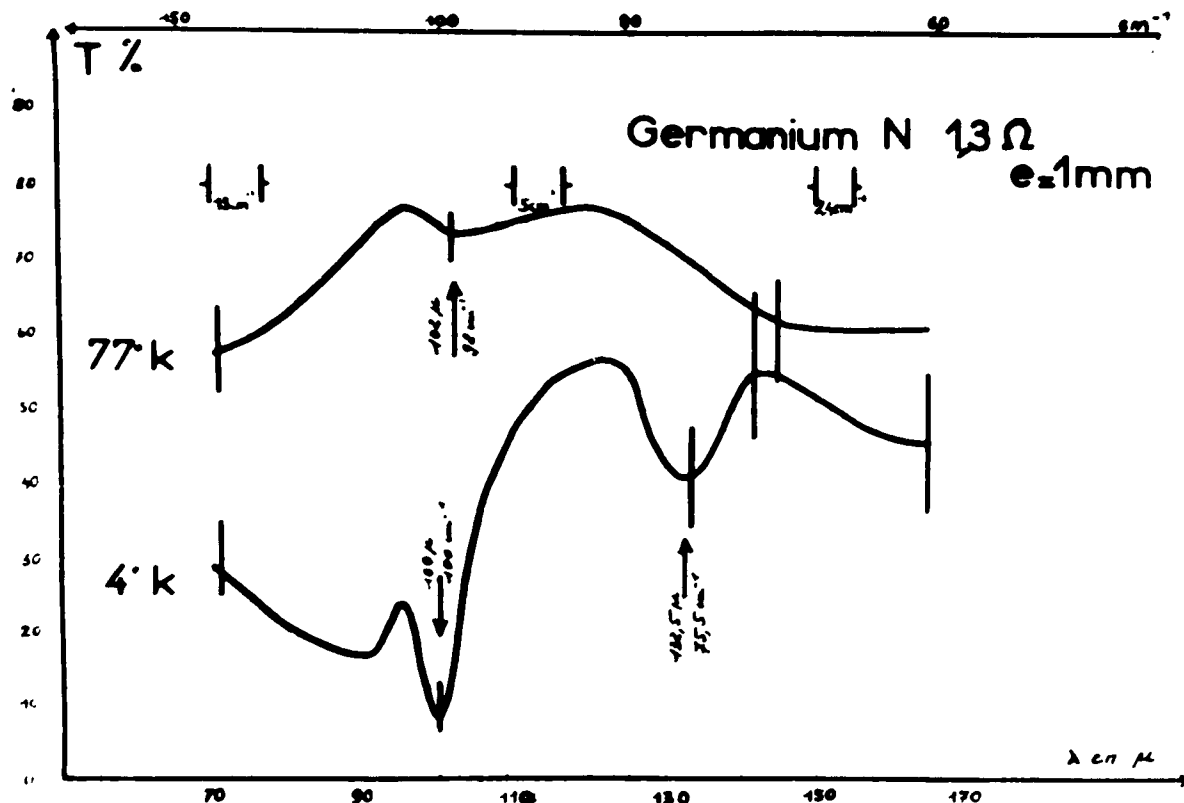


Fig 3

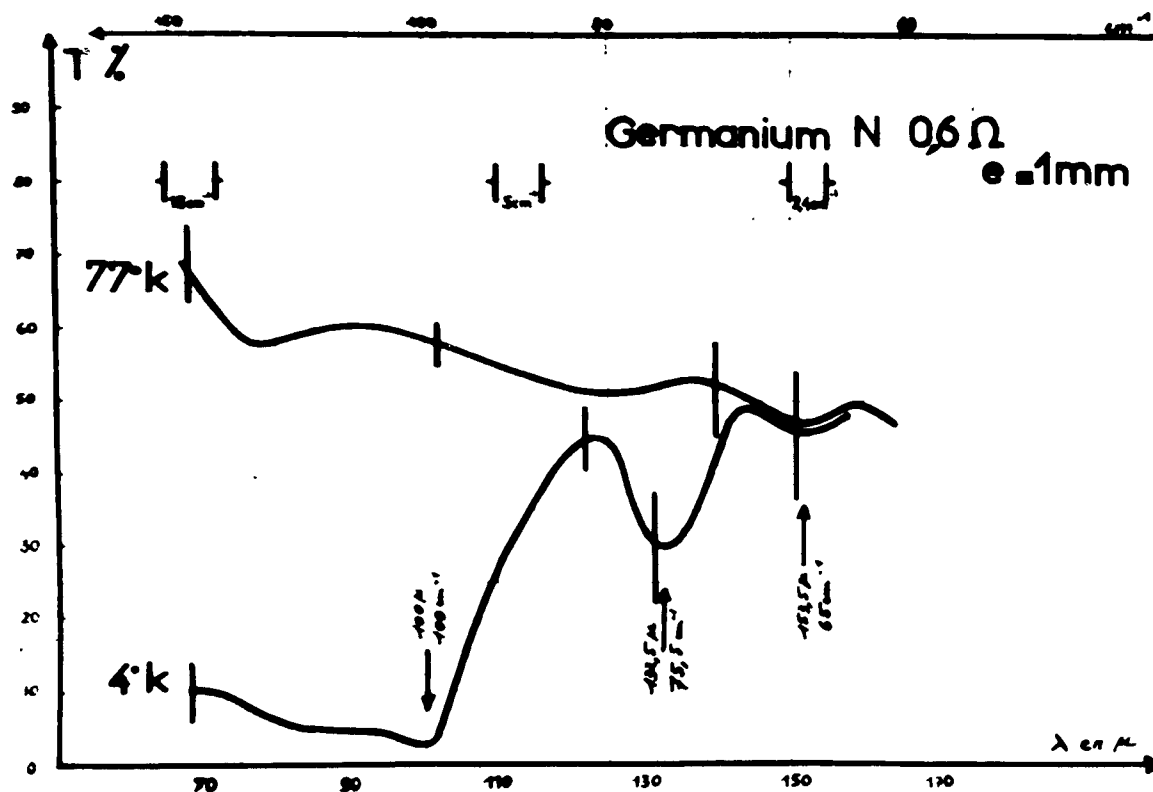


Fig 4

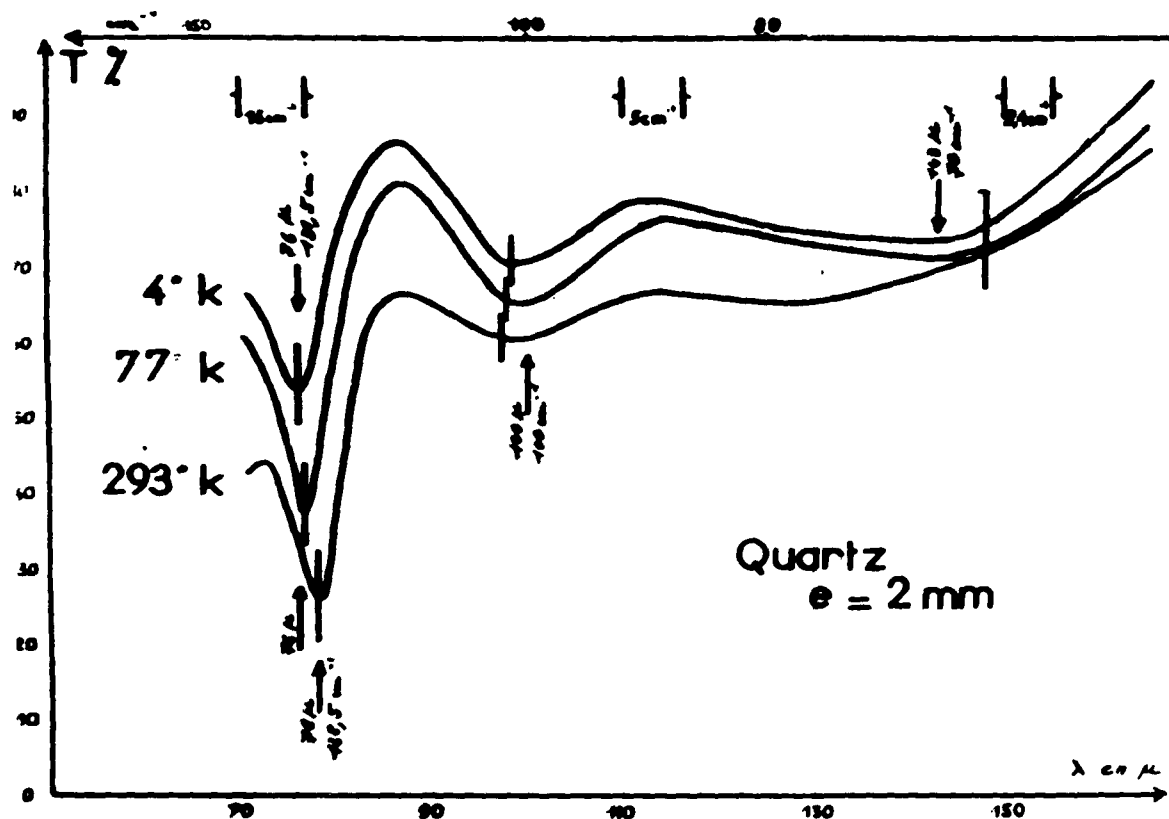


Fig 5.

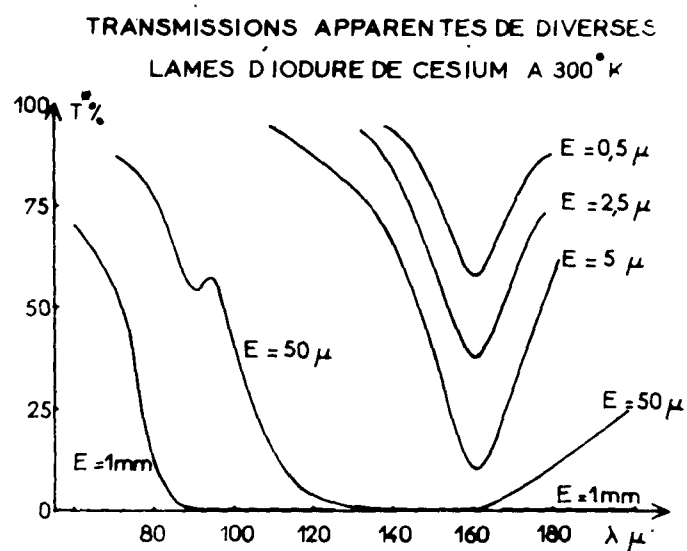
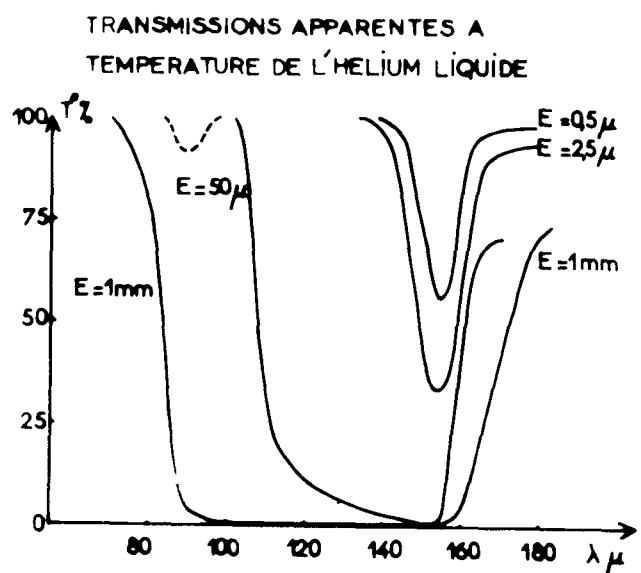
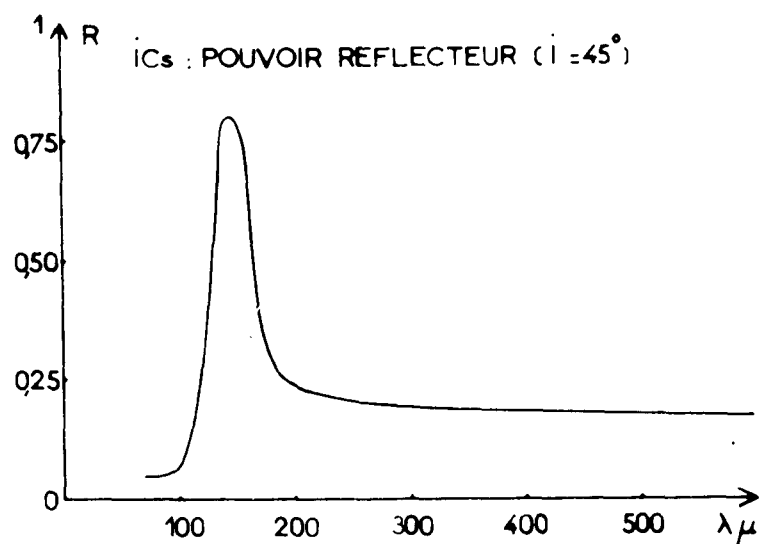
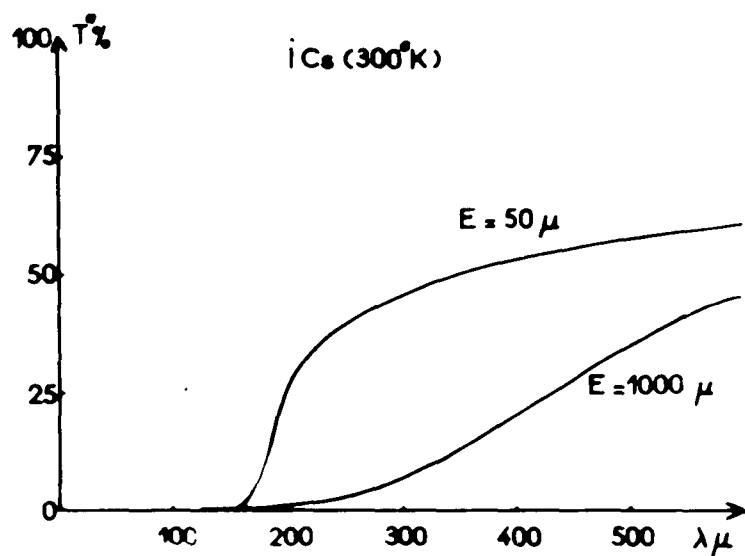


Fig 6

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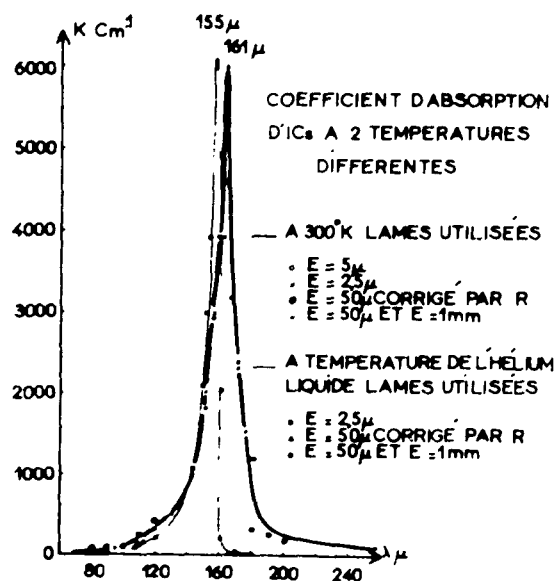


Fig. 10

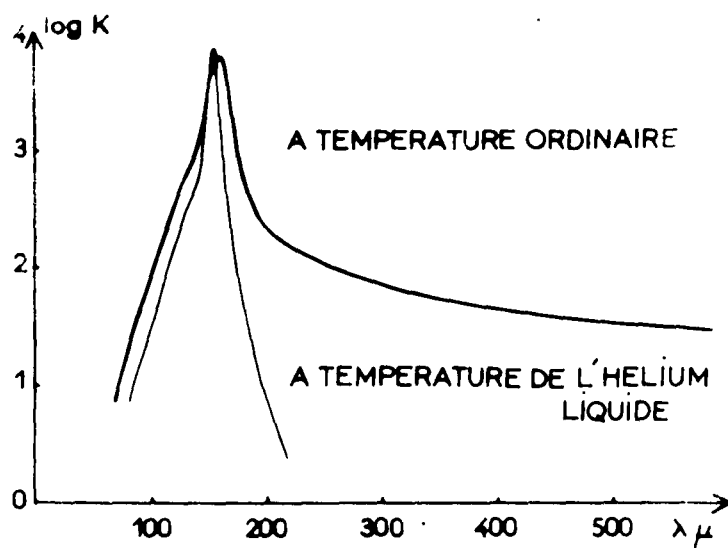


Fig. 11

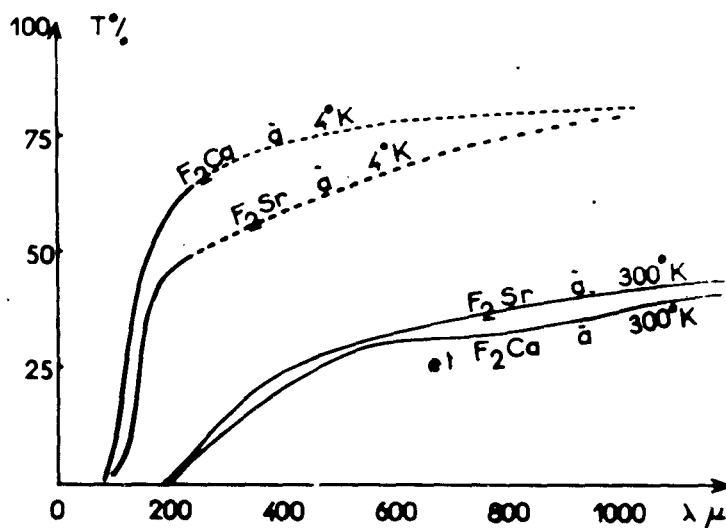


Fig. 12

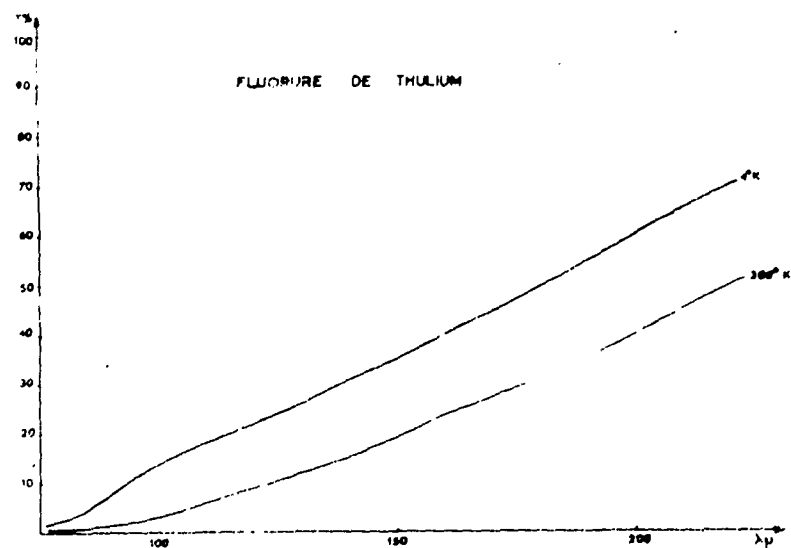


Fig 13

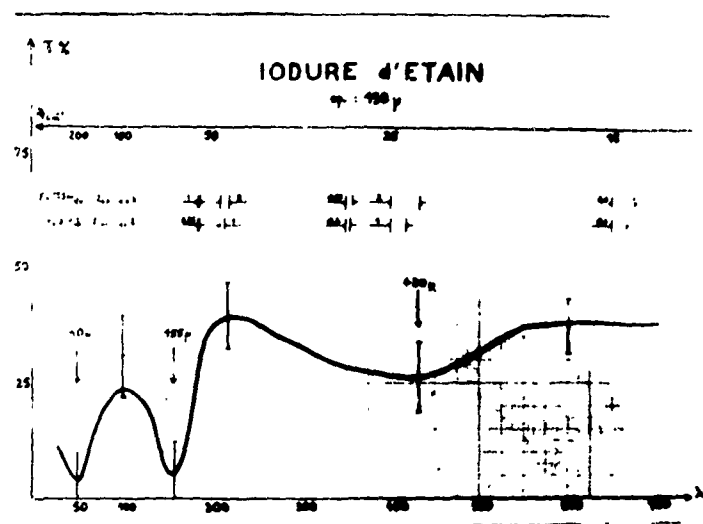


Fig 14

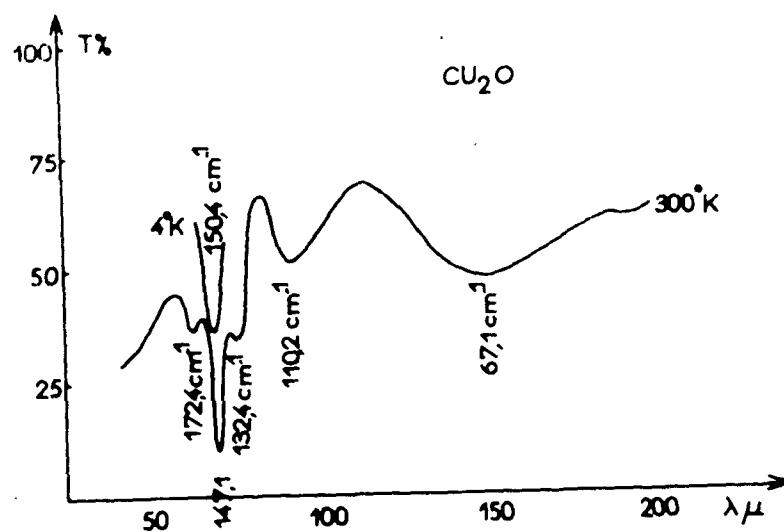


Fig. 15

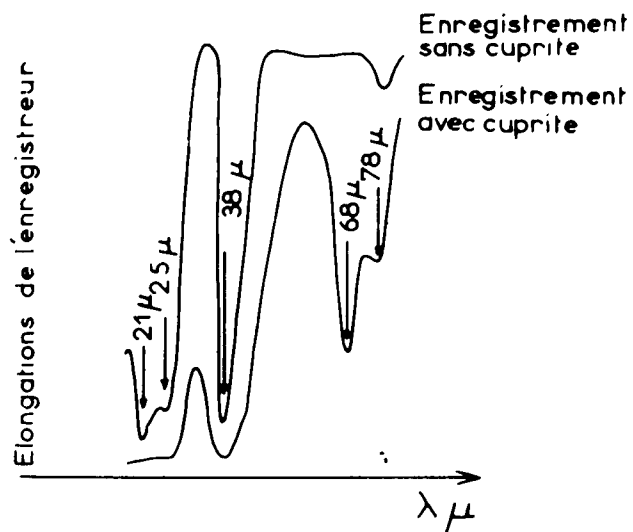


Fig. 16

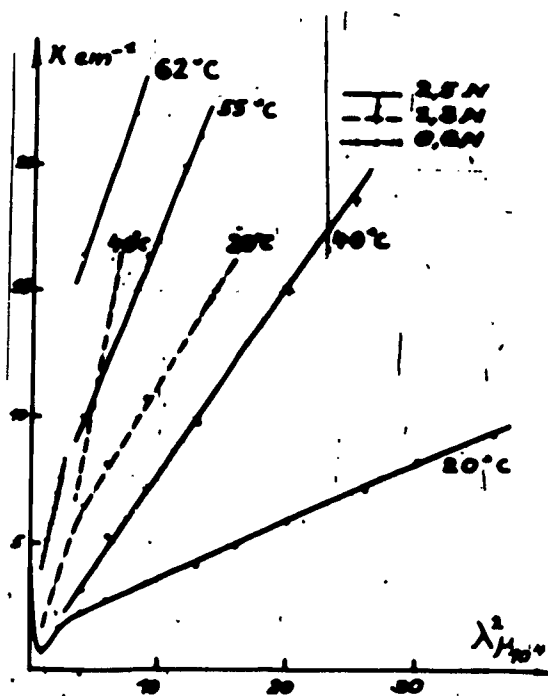


Fig 17

PLAN DU CRYSTAT

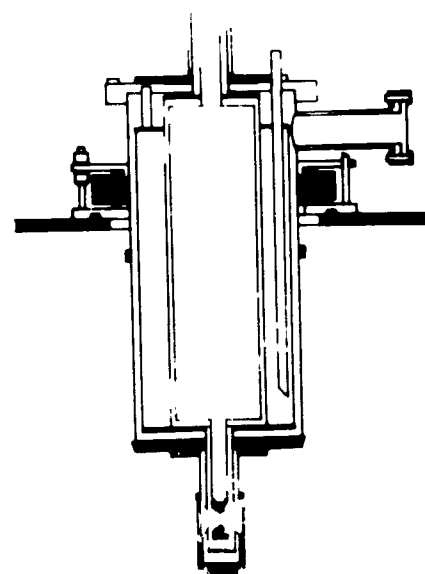


Fig 18

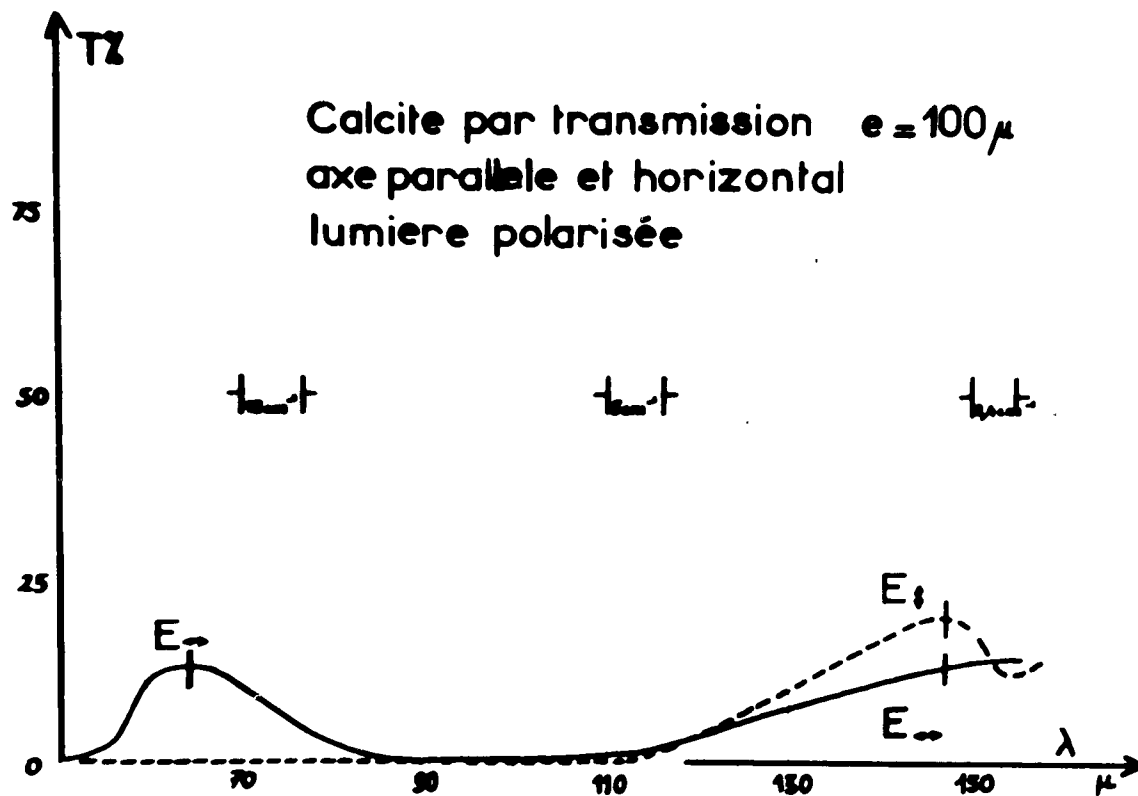


Fig.  
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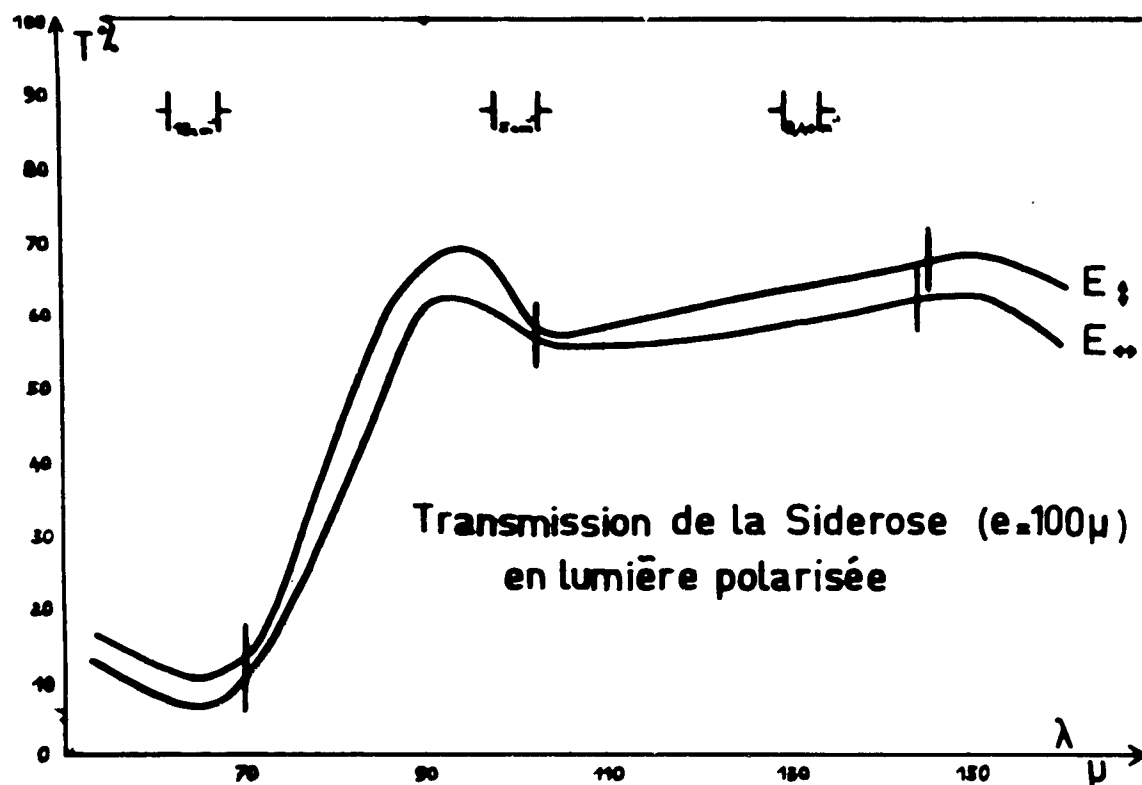


Fig.  
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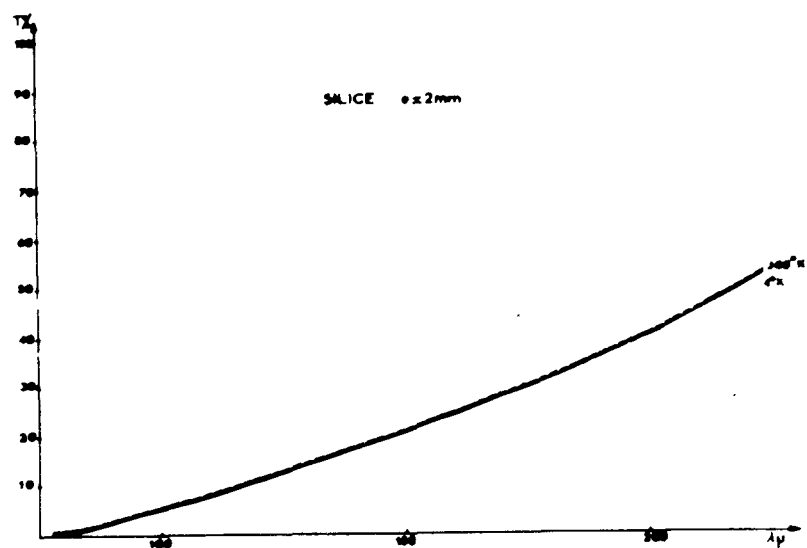


Fig 21

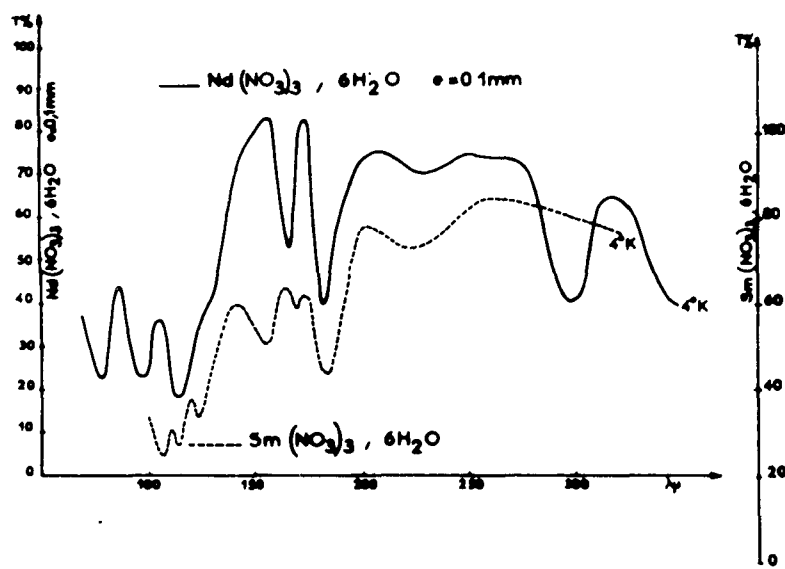


Fig 22

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|--|---|
| <p>GROUP FOR THE ADVANCEMENT OF<br/>SPECTROSCOPIC METHODS<br/>1, rue Gaston-Boissier<br/><u>PARIS</u> / 15ème<br/>(FRANCE)</p> <p>31 May 1963</p> <p>ANNUAL SUMMARY REPORT</p> <p>FAR INFRARED SPECTRA OF CRYSTALS AND SOLIDS IN A LARGE RANGE<br/>OF TEMPERATURE.</p> <p>J. LECOMTE and A. HADNI.</p> <p>ABSTRACT : Far Infrared spectra of 11 solids at liquid<br/>helium temperature and 7 at room temperature.</p> | <p>AF 61 (052) - 518</p> <p>GROUP FOR THE ADVANCEMENT OF<br/>SPECTROSCOPIC METHODS<br/>1, rue Gaston-Boissier<br/><u>PARIS</u> / 15ème<br/>(FRANCE)</p> <p>31 May 1963</p> <p>ANNUAL SUMMARY REPORT</p> <p>FAR INFRARED SPECTRA OF CRYSTALS AND SOLIDS IN A LARGE RANGE<br/>OF TEMPERATURE.</p> <p>J. LECOMTE and A. HADNI.</p> <p>ABSTRACT : Far Infrared spectra of 11 solids at liquid<br/>helium temperature and 7 at room temperature.</p> |
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